

Spectroscopic investigation (FT-IR and FT-Raman), vibrational assignments, HOMO LUMO and NLO analysis of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide

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Abstract

Vibrational spectral analysis of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide was carried out using FT-IR and FT-Raman spectroscopic techniques. The equilibrium geometry and vibrational wave numbers have been computed using density functional B3LYP method with 6-311++G(d,p) as basis set. HOMO–LUMO energy and the thermodynamic parameters are also evaluated. The thermodynamic functions (heat capacity, internal heat energy, Gibbs energy and entropy) from spectroscopic data by statistical methods were obtained for the range of temperature 100–1000 K.

Keyword: Vibrational spectra, DFT, HOMO–LUMO, Thermodynamic functions

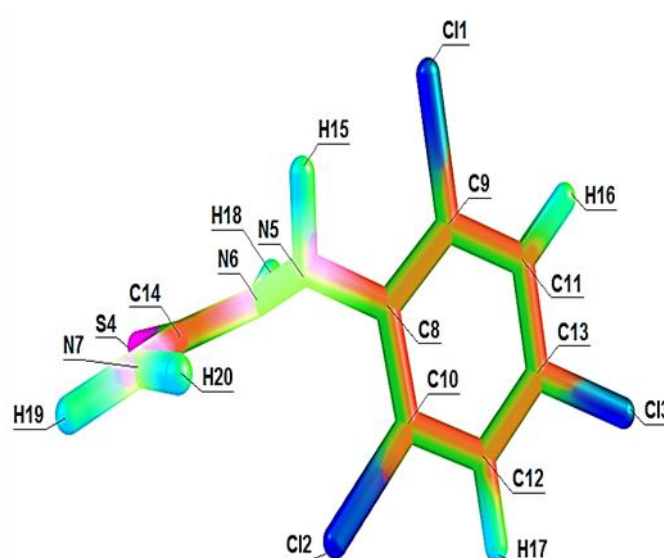


Figure 1. Optimized structure of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide

Introduction

During the earlier periods organic nonlinear optical materials have been attracted much attention because of their optical nonlinearity, fast response, relatively low price, ease of manufacture and integration into devices. NLO materials have gained consideration in recent years with respect to their future potential applications in the field of optoelectronic such as optical communication, computing, switching and dynamic image processing.

H.R. Manjunath *et al*¹ has reported Trichlorophenyls group is the nonlinear optical chalcone derivative, it containing the presence of wide transparency range and third harmonic efficiency and it having luminescence^{2,3,4}.

Hydrazinecarbothioamide complexes are having the antimicrobial activity against⁵, Antifungal activities, Antioxidant studies, Nitric oxide scavenging activity and Hydrogen peroxide scavenging activity⁶.

In the present work aims is to investigate the FTIR, FT-Raman, vibrational assignments of title compound by computationally. In addition the HOMO – LUMO and NLO analysis also carried out.

Computational details

We have utilized Density functional theory (DFT) theory for the computation of molecular structure, vibrational frequencies and energies of optimized structures. Because of considerable effort has been directed to the understanding of organic molecule of theoretical calculations with the DFT⁷ with the Becke's three-parameter hybrid functional⁸ for the exchange part and the Lee–Yang–Parr correlation function⁹, accepted as a cost-effective approach. Therefore, geometrical parameters, FTIR, FT-Raman spectra of the heading molecule (in the ground state) were calculated in tandem with Gaussian09 suite of quantum chemical codes¹⁰.

Results and discussion

Molecular geometry

The optimized structure of **2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide** are shown in the following fig 1. The corresponding minimum energy obtained by **B3LYP/6-311++G (D,P)** method were fall on -2213.6014933. From the optimized geometry the optimized structural parameters are tabulated on Table 1 & 2.

The Geometrical parameters are obtained by computationally. For 1,3,5-Trichlorobenzene ring the Cl-C bond lengths are 1.760, 1.746 and 1.751. For Thiourea group the S₄-C₁₄, N₆-C₁₄ and N₇-C₁₄ bond lengths are 1.674 1.372 and 1.348.

For bond angle of 1,3,5-Trichlorobenzene ring at C₉ position, the angles Cl₁-C₉-C₈ is 119.5°, Cl₁-C₉-C₁₁ is 117.7°. At C₁₀ position, the angles Cl₂-C₁₀-C₈ is 120.2°, Cl₂-C₁₀-C₁₂ is 117.8°. At C₁₃ position, the angles Cl₃-C₁₃-C₁₁ is 119.5° and Cl₃-C₁₃-C₁₂ is 119.5°.

For bond angle of thiourea group at C₁₄ position, the angles S₄-C₁₄-N₆ is 120.0°, S₄-C₁₄-N₇ is increased by 124.3° and this asymmetry reveals the interaction between the thiol group. For urea group S₄-C₁₄-N₇ is increased by 4.3° N₆-C₁₄-N₇ is reduces by 4.4° and symmetry reveals the urea group.

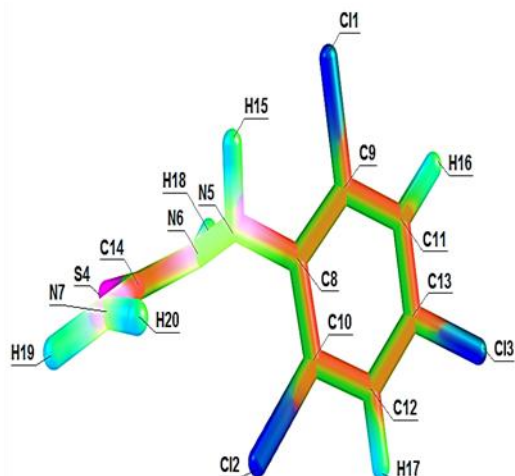


Figure 1. Optimized structure of
2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide

Atom. No	Atom	Atom. No	Atom
1	Cl	11	C
2	Cl	12	C
3	Cl	13	C
4	S	14	C
5	N	15	H
6	N	16	H
7	N	17	H
8	C	18	H
9	C	19	H
10	C	20	H

Table 1: Atoms and position numbers of
2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide

Vibrational analysis

The observed IR, Raman bands and calculated wavenumbers and assignments are given in Table 3 and spectres are given in Figure 2 & 3 the Trichlorobenzene ring C-Cl stretching¹¹ modes occur between 600 cm⁻¹ to 800 cm⁻¹.

For thiourea group C=S stretching vibration has been assigned by various authors to frequencies ranging from less than 800 cm⁻¹ to greater than 1 500 cm⁻¹. The region of absorption for the C=S vibration^{12,13,14} obviously depends on the type of compound in which this group occurs, specifically on what atoms are bonded to the carbon atom of the thiocarbonyl group, where nitrogen atoms are attached to the thiocarbonyl derivatives, there seem to be three regions in the infrared in which a C=S vibration, coupled with other vibrations, may be observed. This appears to be a useful concept, although, of the three arbitrary regions, viz. 1 570 - 1 395 cm⁻¹, 1 420 - 1 260 cm⁻¹, and 1 140 - 940 cm⁻¹, the lowest should be extended to 700 cm⁻¹ to include absorptions which have recently been shown to exhibit a contribution from C=S stretching.

The identification of C-N^{12,13,14} vibrations is found to be difficult tasks because of the mixing of several vibrations possible in this region.

The thiourea which is under investigation has NH_2 group¹⁵ and hence asymmetric and symmetric NH stretch vibrations are possible. The NH stretching frequency of aromatic compounds occurs in the region $3300\text{--}3500\text{ cm}^{-1}$ are assigned to NH_2 asymmetric and symmetric group of vibrations. The bands at 3460 cm^{-1} and 3380 cm^{-1} are due to N-H stretching modes of vibrations appear in group are found to be stronger when compared to N-H ring vibrations.

The C-C stretch vibrations¹⁶ occur nearly at 1600 cm^{-1} . The peak observed at 1710 cm^{-1} is due to C=C stretching vibrations¹⁶.

Bond length	value	Bond angle	value	Bond angle	value
Cl ₁ -C ₉	1.760	Cl ₁ -C ₉ -C ₈	119.5	C ₉ -C ₈ -C ₁₀	116.4
Cl ₂ -C ₁₀	1.746	Cl ₁ -C ₉ -C ₁₁	117.7	C ₈ -C ₉ -C ₁₁	122.8
Cl ₃ -C ₁₃	1.751	Cl ₂ -C ₁₀ -C ₈	120.2	C ₈ -C ₁₀ -C ₁₂	122.0
S ₄ -C ₁₄	1.674	Cl ₂ -C ₁₀ -C ₁₂	117.8	C ₉ -C ₁₁ -C ₁₃	118.5
N ₅ -N ₆	1.407	Cl ₃ -C ₁₃ -C ₁₁	119.5	C ₉ -C ₁₁ -H ₁₆	120.4
N ₅ -C ₈	1.415	Cl ₃ -C ₁₃ -C ₁₂	119.5	C ₁₀ -C ₁₂ -C ₁₃	119.2
N ₅ -H ₁₅	1.016	S ₄ -C ₁₄ -N ₆	120.0	C ₁₀ -C ₁₂ -H ₁₇	119.9
N ₆ -C ₁₄	1.372	S ₄ -C ₁₄ -N ₇	124.3	C ₁₃ -C ₁₁ -H ₁₆	121.1
N ₆ -H ₁₈	1.013	N ₆ -N ₅ -C ₈	115.5	C ₁₁ -C ₁₃ -C ₁₂	121.1
N ₇ -C ₁₄	1.348	N ₆ -N ₅ -H ₁₅	110.7	C ₁₃ -C ₁₂ -H ₁₇	120.8
N ₇ -H ₁₉	1.006	N ₅ -N ₆ -C ₁₄	121.5	N ₅ -N ₆ -H ₁₈	118.9
N ₇ -H ₂₀	1.010			C ₈ -N ₅ -H ₁₅	111.0
C ₈ -C ₉	1.405			N ₅ -C ₈ -C ₉	121.3
C ₈ -C ₁₀	1.406			N ₅ -C ₈ -C ₁₀	122.2
C ₉ -C ₁₁	1.389			C ₁₄ -N ₆ -H ₁₈	115.7
C ₁₀ -C ₁₂	1.390			N ₆ -C ₁₄ -N ₇	115.6
C ₁₁ -C ₁₃	1.388			C ₁₄ -N ₇ -H ₁₉	117.5
C ₁₁ -H ₁₆	1.081			C ₁₄ -N ₇ -H ₂₀	120.1
C ₁₂ -C ₁₃	1.390			H ₁₉ -N ₇ -H ₂₀	120.3

Table 2: Bond angle and bond Length of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide

Frequency	IR intensity	Raman intensity	Assignment	Frequency	IR intensity	Raman intensity	Assignment
602.0027	2.5774	2.2046	C-Cl Stretch	1264.812	89.4942	32.7947	C-N Stretch
645.159	6.5066	2.052	C-Cl Stretch	1286.1476	256.8435	15.7995	C-N Stretch
717.2765	27.425	1.6743	C-Cl Stretch	1294.1433	8.6448	19.8999	C-N Stretch
748.0758	59.0324	1.3823	C-Cl Stretch	1464.783	92.9653	35.5629	C=S Stretch
788.1781	58.1018	1.8799	C-Cl Stretch	1539.0082	206.7108	9.202	N-H Bending
834.2012	37.1541	4.8443	C=S Stretch	1600.2104	47.2596	16.369	C-C Stretch
1021.5299	81.0566	14.3217	C=S Stretch	1608.7181	71.7877	73.8122	C=C Stretch
1618.9863	149.3716	62.0652	C=C Stretch	3556.1126	35.1922	80.5028	N-H Stretch
3500.6855	21.5623	114.744	N-H Stretch	1618.9863	149.3716	62.0652	C=C Stretch

Table 3: Vibrational assignments of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide

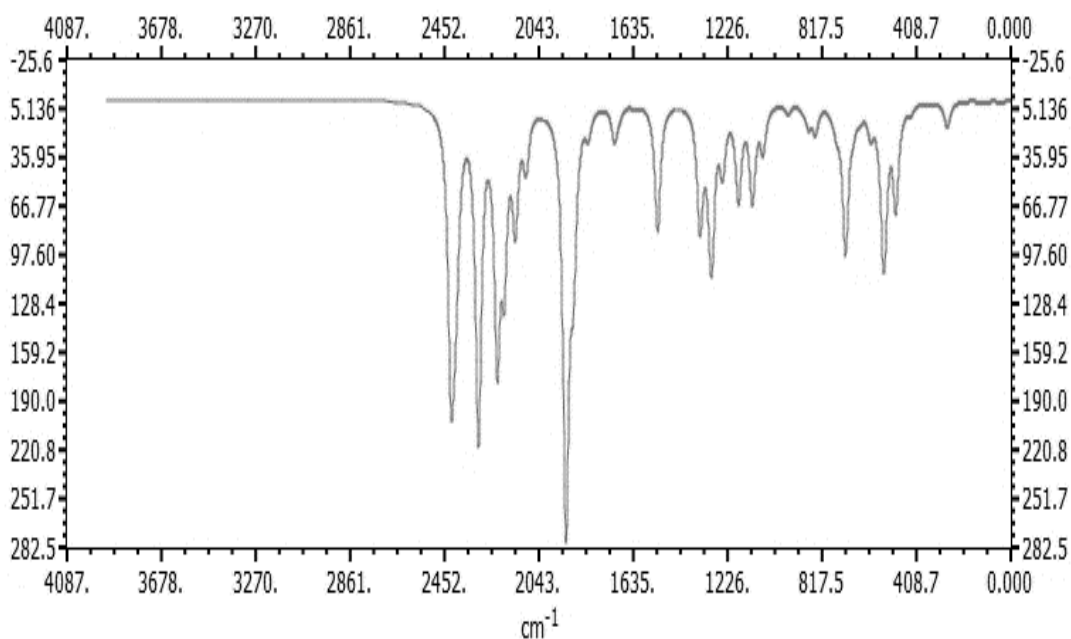


Figure 2: FTIR Theoretical spectrum of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide

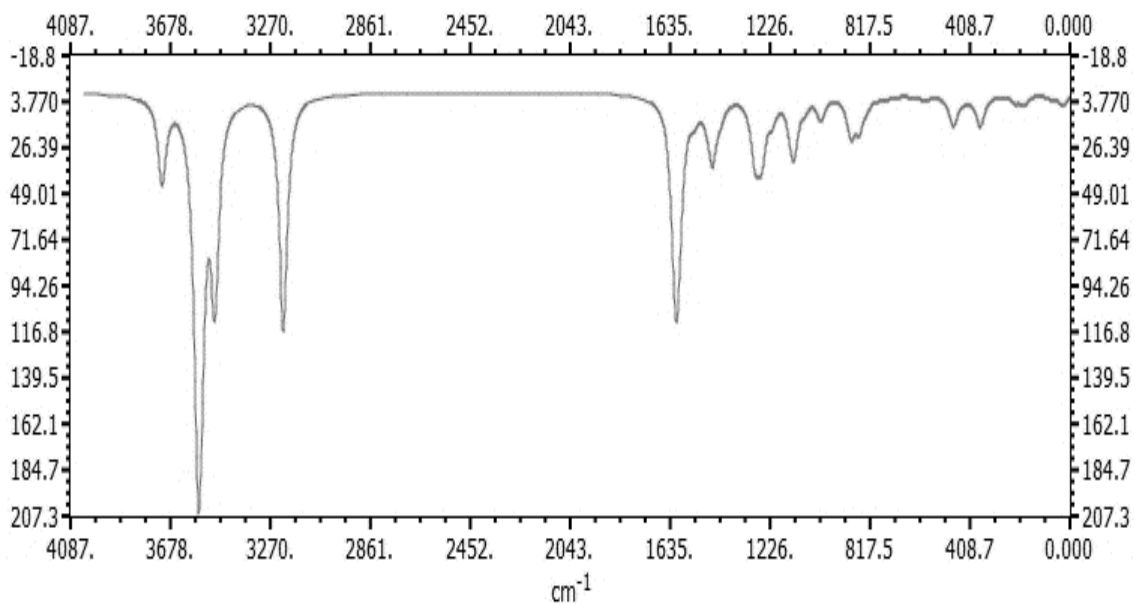


Figure 3: FT-RAMAN Theoretical spectrum of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide

HOMO-LUMO analysis

The concepts of aromaticity, HOMO, and LUMO are of fundamental importance in understanding the chemical stability and reactivity of many organic molecules. Molecular orbital and their properties like energy is very useful to the physicists and chemists and their frontier electron density is used for predicting the most reactive position in p electron system and also explains several types of reaction in conjugated systems¹⁷. The frontier orbitals of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide are plotted in Figure. 4. The molecular orbital calculations indicate that the title compound has 30 occupied molecular orbitals. The HOMO – LUMO energy gap of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide was calculated.

$$\begin{aligned}\text{HOMO energy (HF/sto-3g*)} &= -0.14908 \text{ au} \\ \text{LUMO energy (HF/sto-3g*)} &= 0.18742 \text{ au} \\ \text{HOMO-LUMO energy gap} &= 0.3365 \text{ au}\end{aligned}$$

The HOMO is located over the sulphur atom and Trichlorophenyl groups attached to the 2,4,6 Trichlorophenyl ring. The HOMO→LUMO transition implies an electron density transfer from sulphur atom to 2,4,6 Trichlorophenyl ring. Moreover, these orbital significantly overlap in their position for 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide as shown in Figure 4. The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

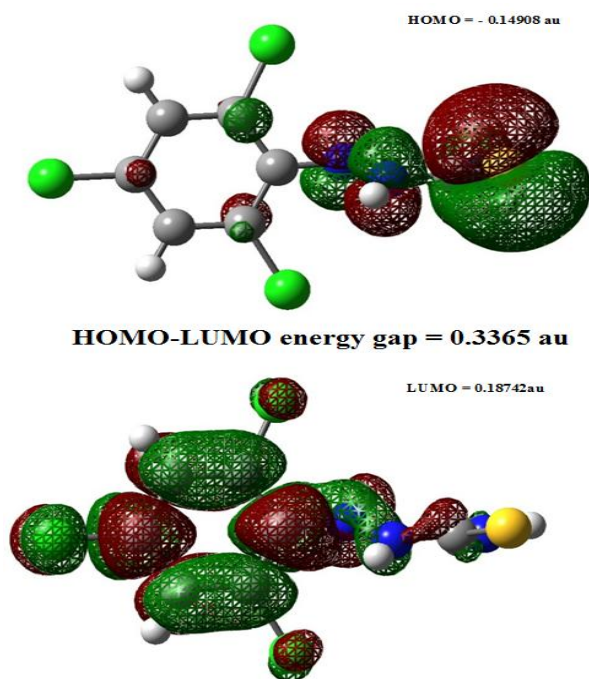


Figure 4: HOMO, LUMO energy and its energy gap

Predication of first hyperpolarizability

The first hyperpolarizability(β_o) of the title complexes is calculated and the related properties (β_o, α_o) were calculated using the B3LYP/6-311++G(D,P) basis set, based on the finite field approach. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field.

Theoretically calculated values of hyperpolarizability(β_o) are $1350.098209 \times 10^{-33}$ esu as shown in the Table 4. We can conclude that the title complex is an attractive object for future studies of non-linear optical application.

Parameters	B3LYP/6-311++G(D,P)
β_{xxx}	868.1230255
β_{xyx}	849.3601229
β_{xyy}	-711.1855622
β_{yyy}	-994.3892322
β_{xxz}	-161.9250599
β_{xyz}	-478.9959876
β_{yyz}	251.8511742
β_{xzz}	493.2862624
β_{yzz}	-492.8094966
β_{zzz}	906.6360737
β_o esu	$1350.098209 \times 10^{-33}$ esu

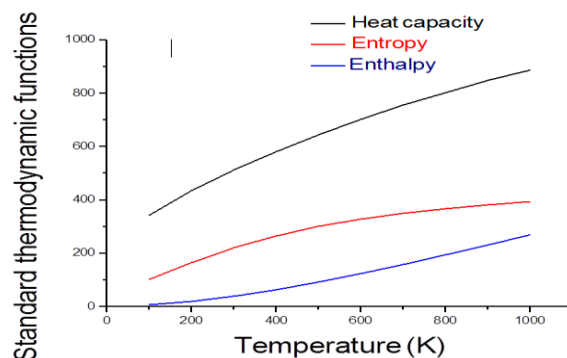
Table 4: β components and first order hyperpolarizability β_o (in esu) value

Thermo dynamical properties

On the basis of vibrational analyses and statistical thermodynamics, the standard thermodynamic functions: heat capacity ($C_{p,m}^0$), entropy (S_m^0) and enthalpy (H_m^0) were calculated using perl script THERMO.PL¹⁸ and are listed in Table 5. From the table the graph is drawn taking standard thermodynamic functions are in x axis and Temperature (K) in y axis. As observed from Table & Graph, the values of $C_{p,m}^0, S_m^0$ and H_m^0 all increase with the increase of temperature from 100 to 1000 K, which is attributed to the enhancement of the molecular vibration as the temperature increases.

T(K)	S (J/mol.K) S_m^0	Cp (J/mol.K) $C_{p,m}^0$	ddH (kJ/mol) H_m^0
100.00	343.20	101.72	6.66
200.00	434.03	166.27	20.13
298.15	510.75	219.99	39.17
300.00	512.11	220.91	39.58
400.00	582.05	265.80	63.99
500.00	645.34	301.35	92.42
600.00	702.83	328.97	124.00
700.00	755.23	350.58	158.02
800.00	803.21	367.83	193.97
900.00	847.37	381.90	231.48
1000.00	888.23	393.60	270.27

Table 5. The thermodynamic values



Graph 1: Graphical representation of thermodynamic properties

Consolation

FTIR and FT-Raman spectra of 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide are recorded and the detailed vibrational assignments were presented. The molecular geometry, vibrational frequencies, infrared intensities and Raman scattering activities of the molecules had been calculated by using DFT (B3LYP) method with 6-311++G(d,p) basis set. The calculated HOMO and LUMO energies show that charge transfer occur the molecule and other halogen substituted. The results are of assistance in the theoretical evidence for 2-(2,4,6-Trichlorophenyl) hydrazinecarbothioamide in reaction intermediates, non-linear optical and photoelectric materials.

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